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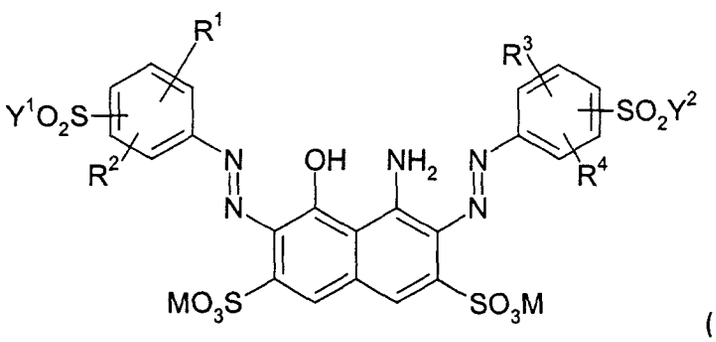
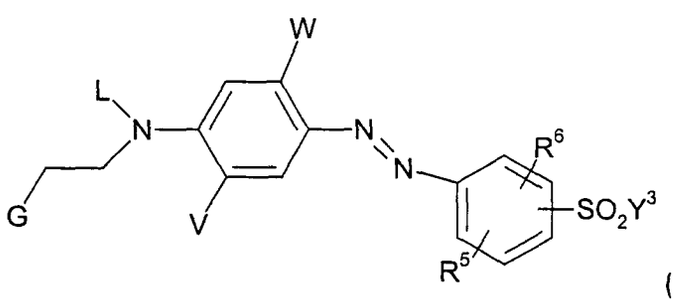
(54) Deep black dye mixtures of fiber-reactive azo dyes

(57) The present invention claims a dye mixture comprising at least one dyestuff of the general formula (1)



(1)

and at least one dyestuff of the general formula (2)



(2)

where
M, Y^1, Y^2, Y^3, R^1, R^2, R^3, R^4, R^5, R^6, W, V, L and G are defined as given in claim 1, a process for its preparation and

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its use for dyeing and printing hydroxyl-and/or carboxamido-containing material.

Description

[0001] The present invention relates to the field of fiber-reactive dyes.

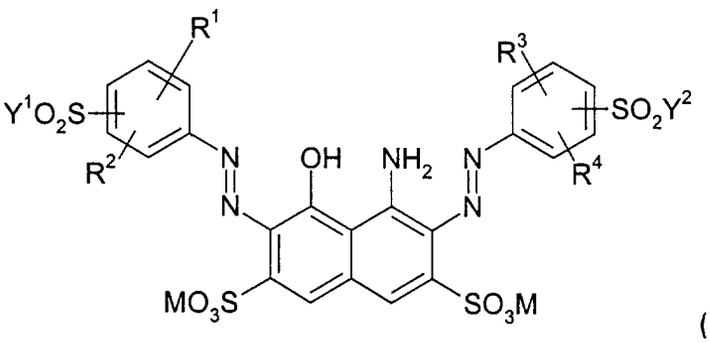
[0002] Black-dyeing mixtures of fiber-reactive dyes are known from US 5,445,654 and US 5,611,821 as well as from KR 94-2560-B1. Deep black dye mixtures are known, for example, from JP-A Sho-58-160 362 which are based on a navy-blue disazo dye and an orange monoazo dye. However, these dye mixtures have some deficiencies, in particular the washfastness to repeated washings is unfavorable.

[0003] Dyes according to the general formula (1) below are already known from, for example, US 2,657,205, JP-A Sho-58-160 362 and US 4,257,770 and the references cited therein.

Monoazo dyes of the general formula (2) below are already known as well, for example from DE-A 3537260, JP-A 7406798, JP-A 4950291, DE-A 2351970, DE-A 2362 683, BE-A 861220 and US 4,283,196. However, these orange dyes generally have poor wash and chlorine fastnesses and do not build up well.

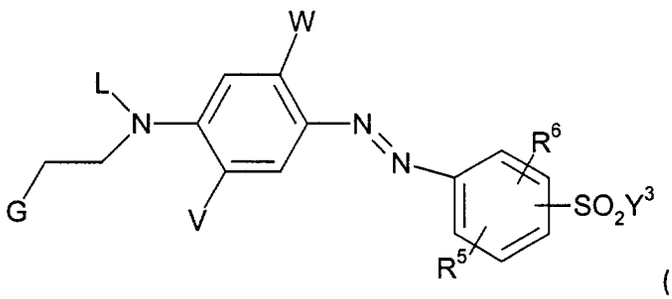
[0004] The inventors of the present invention have surprisingly found now that the washfastness and build up properties of deep black dye mixtures according to the documents mentioned above can be improved by replacing their orange components by the monoazo dyes of the general formula (2). As the washfastness properties of said deep black dye mixtures are generally limited by the washfastness of the orange component, a skilled person would not have expected that dyes of the general formula (2) would be suitable for improving such properties in view of their disadvantages when used individually.

[0005] The present invention claims dye mixtures comprising one or more dyestuffs of the general formula (1)



(1)

and one or more dyestuffs of the general formula (2)



(2)

where

M	is an alkali metal, an ammonium or the equivalent of an alkaline earth metal;
Y^1, Y^2 and Y^3	are independently ethenyl or a grouping of the formula $-CH_2CH_2Z$, where
Z	is an alkali-eliminable grouping;
R^1, R^2, R^3, R^4, R^5 and R^6	are independently hydrogen, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, sulfo or chloro;
W	is hydrogen, chloro, bromo, nitro, amino, acetamido, benzamido, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, hydroxy, ureido or (C_2-C_4)-alkanoyl;
V	is hydrogen, chloro, bromo, nitro, amino, acetamido, benzamido, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, hydroxy, ureido or (C_2-C_4)-alkanoyl;

L	is hydrogen, methyl, ethyl or is ethyl which is substituted in the β-position by G;
G	is cyano, hydroxy, sulfo, sulfato, phosphato, acetyloxy or a residue of a lower polyethylenepolyether.

[0006] Preference is given to dye mixtures including from 60 to 95%by weight of one or more dyestuffs of the general formula (1) and from 5 to 40%by weight of one or more of a dyestuff of the general formula (2), based on the weight of the dye mixture. Special preference is given to dye mixtures including from 65 to 90% by weight of one or more dyestuffs of the general formula (1) and from 10 to 35%by weight of one or more dyestuffs of the general formula (2), based on the weight of the dye mixture.

[0007] A (C_1-C_4)-alkyl grouping standing for R^1 to R^6, W or V may be straight-chain or branched and be for example methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl or tert-butyl. Preference is given to methyl and ethyl. The same logic rules for (C_1-C_4)-alkoxy groups, which are thus preferably methoxy and ethoxy. A (C_2-C_5)-alkanoyl grouping standing for W or V is preferably acetyl or propionyl. A residue of a lower polyethylenepolyether is preferably a residue of the formula CH_3CH_2-$(OCH_2CH_2)_n$-O- with n = 2-10.

[0008] Alkali metal M is preferably sodium, potassium or lithium, particularly preferably sodium. The equivalent of an alkaline earth metal M is preferably the equivalent of calcium.

An alkali-eliminable grouping Z is, for example, chloro, thiosulfato, phosphato, (C_2-C_5)-alkanoyloxy, such as acetyloxy, sulfobenzoyloxy or p-toluylsulfonyloxy and is preferably sulfato.

The groups "sulfo", "thiosulfato", "phosphato" and "sulfato" include both the acid form and the salt form of these groups. Accordingly, sulfo groups are groups of the formula $-SO_3M$, thiosulfato groups are groups of the formula $-S-SO_3M$, phosphato groups are groups of the formula $-OPO_3M_2$ and sulfato groups are groups of the formula $-OSO_3M$, in which M is defined as above.

The groups $—SO_2Y^1$, $-SO_2Y^2$ and $—SO_2Y^3$ are preferably disposed para or meta relative to the diazo group, particularly preferably para. Y^1, Y^2 and Y^3 are preferably ethenyl or β-sulfatoethyl.

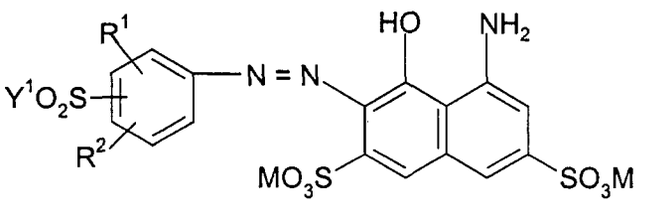
R^1 is preferably hydrogen, methoxy or sulfo, R^2 is preferably hydrogen, methyl or methoxy and R^3 and R^4 are preferably hydrogen. R^5 and R^6 are preferably hydrogen, methyl, methoxy or sulfo.

[0009] W is preferably hydrogen, chloro, nitro, amino, acetamido, methyl or ureido, V is preferably hydrogen or methoxy.

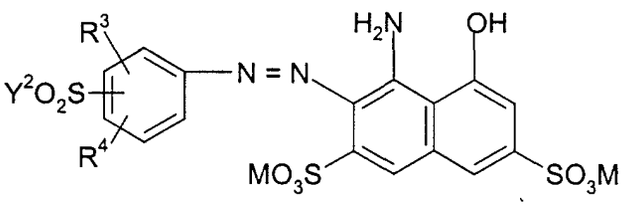
L is preferably hydrogen, ethyl, β-sulfatoethyl, β-hydroxyethyl or β-cyanoethyl, G is preferably sulfato, hydroxy or cyano.

[0010] In preferred dye mixtures according to the present invention, R^1 is hydrogen, methoxy or sulfo, R^2 to R^6 are hydrogen, $—SO_2Y^1$, $-SO_2Y^2$ and $—SO_2Y^3$ are disposed para relative to the diazo group, Y^1, Y^2 and Y^3 are β-sulfatoethyl and W, V, L and G have one of the preferred meanings given above.

[0011] The dye mixtures of the present invention may optionally contain one or more dyestuffs of the general formulae (3a) or (3b) or both



(3a)



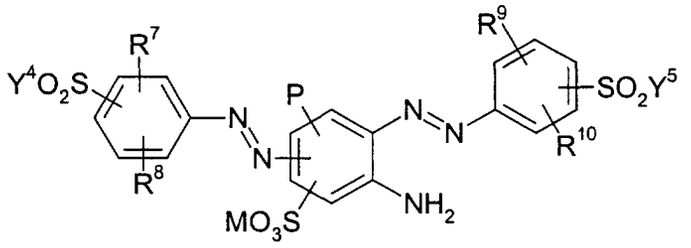
(3b)

in which R^1, R^2, R^3, R^4, M, Y^1 and Y^2 are defined as above. These two dyestuffs may already be formed during the synthesis of the dyestuff of the general formula (1) if coupling reactions of the starting compounds are incomplete.

[0012] If the dye mixture of the present invention contains, as a further component, a dyestuff of formula (3a) or of

formula (3b) or both, the dyestuff or dyestuffs of formula (3a) or of formula (3b) or of both are present in the dye mixture of the dyestuffs of the general formulae (1) and (2) in the range of 0.01 to 8 % by weight, calculated on the 100 % dye mixture of the dyestuffs of the general formulae (1) and (2).

[0013] The dye mixtures of the present invention may in addition contain further dyestuffs which act as so-called shading components. Such shading components are in particular red or yellow to golden orange dyestuffs. They may be contained in a ratio of up to 25 % by weight of the total mixtures. Preferably, they are contained in amounts of 0,5 to 20 % by weight, particularly preferably in amounts of 1 to 10 % by weight, based on the weight of the dye mixture. These shading components are generally used to give the dyeings a more or less reddish or greenish shade and are also added to enhance the shade reproducibility of production batches. Preference is given to dyestuffs of the general formulae (4) to (10)



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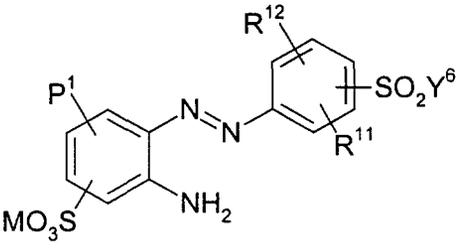

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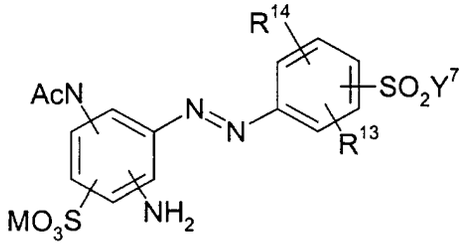

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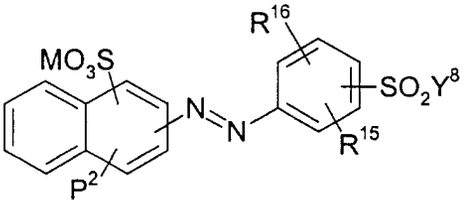

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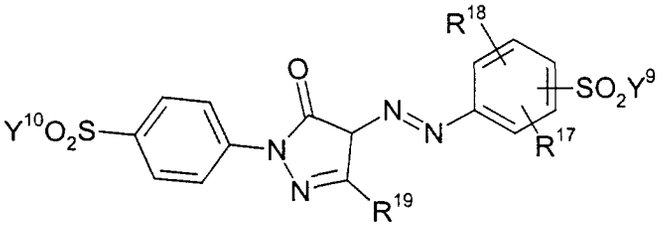

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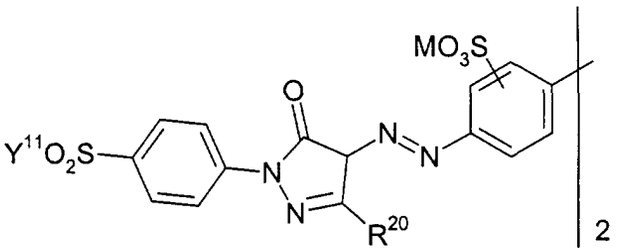

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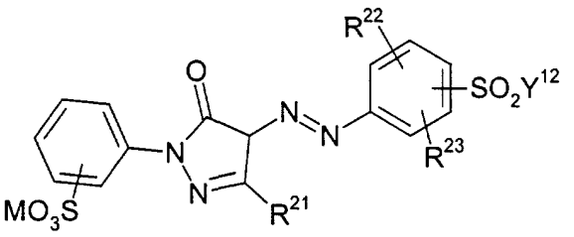


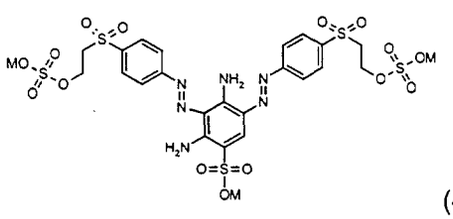
(10)

where

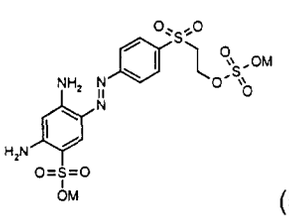
M	is defined as given above;
Y^4 to Y^{12}	independently have one of the meanings of Y^1;
R^7 to R^{18} and R^{22} and R^{23}	independently have one of the meanings of R^1;
R^{19} to R^{21}	are independently (C_1-C_4)-alkyl, -COOH or —$COOR^{24}$, where
R^{24}	is (C_1-C_4)-alkyl; and

P to P^2 are independently hydroxy, (C_1-C_4)-alkoxy, amino, (C_1-C_4)-alkylamino or di-(C_1-C_4)-alkylamino.

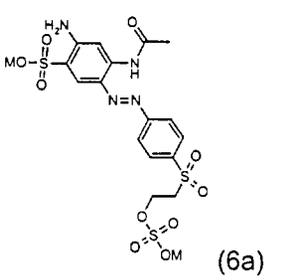
[0014] Especially preferred shading components are the dyestuffs of the formulae (4a), (5a), (6a), (7a), (7b) and (8a)



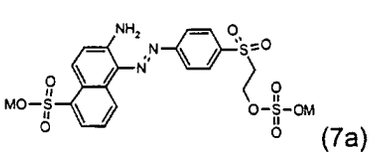
(4a)



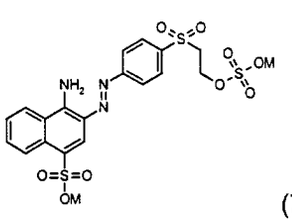
(5a)



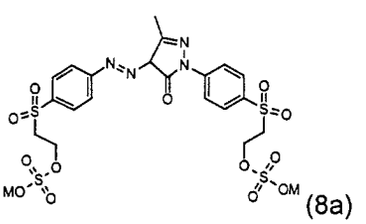
(6a)



(7a)



(7b)



(8a)

wherein M is defined as given above.

The dyestuffs of the general formulae (4) to (10) are known. The dyestuffs of the general formula (4) are described in DE-A 4329421, the dyestuffs of the general formula (5) in JP-A 69-14107, the dyestuffs of the general formula (6) in DE-A 3134357, the dyestuffs of the general formula (7b) in DE-A 1911427, the dyestuffs of the general formula (8) in EP-A 489360, the dyestuffs of the general formula (9) in DE-A 1911427 and the dyestuffs of the general formula (10) in DE-A 1215282.

[0015] The dyestuffs of the general formulae (1) to (10), in particular if those corresponding to the same general formula have the same chromophore, can have, within the meaning of their Y-moiety, structurally different fiber-reactive groups corresponding to their -SO_2-Y-moiety. In particular, the dye mixture can contain dyestuffs of the same chromophore conforming to the general formula (1) and/or dyestuffs of the same chromophore conforming to general formula (2), optionally likewise of the general formulae (3a), (3b) and (4) to (10) in which the fiber-reactive groups of the corresponding -SO_2-Y-moiety are partly vinylsulfonyl groups and partly groups in which the Y-moiety is a β-ethyl substituted group as defined above, such as β-chloroethylsufonyl, β-thiosulfatoethylsulfonyl or, preferably, β-sulfatoethylsulfonyl groups. If the dye mixtures contain the respective dyestuff components in the form of a vinylsulfonyl dye, the proportion of the respective vinylsulfonyl dyestuff to the respective dyestuff with a Y-moiety being a β-ethyl substituted group as defined above, such as a β-chloro- or β-thiosulfato- or β-sulfatoethyl-sulfonyl dye, will be up to about 30 mol-%, based on the respective dyestuff chromophore. Preference is here given to the dye mixtures in which the proportion of vinylsulfonyl dyestuff to said β-substituted ethylsulfonyl dyestuff, such as β-sulfatoethylsulfonyl dyestuff, is in terms of the molar ratio between 2 : 98 and 30 : 70.

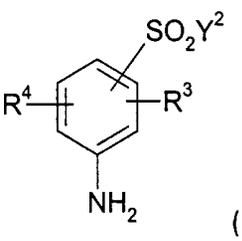
[0016] The dye mixtures of the present invention can be present as a preparation in solid or liquid (dissolved) form. In solid form they generally contain the electrolyte salts customary in the case of water-soluble and in particular fiber-reactive dyes, such as sodium chloride, potassium chloride and sodium sulfate, and also the assistants customary in commercial dyes, such as buffer substances capable of establishing a pH in aqueous solution between 3 and 7, such as sodium acetate, sodium borate, sodium bicarbonate, sodium citrate, sodium dihydrogenphosphate and disodium hydrogenphosphate, small amounts of siccatives or, if they are present in liquid, aqueous solution (including the presence of thickeners of the type customary in print pastes), substances which ensure the permanence of these preparations, for example mold preventatives.

[0017] In general, the dye mixtures of the present invention are present as dye powders containing 10 to 80% by weight, based on the dye powder or preparation, of a strength-standardizing colorless diluent electrolyte salt, such as those mentioned above. These dye powders may additionally include the aforementioned buffer substances in a total amount of up to 10%, based on the dye powder. If the dye mixtures of the present invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, for example between 5 and 50% by weight, and the electrolyte salt content of these aqueous solutions will preferably be below 10% by weight, based on the aqueous solutions. The aqueous solutions (liquid preparations) may include the aforementioned buffer substances in an amount which is generally up to 10% by weight, for example 0.1 to 10% by weight, preference being given to up to 4% by weight, especially 2 to 4% by weight.

[0018] The present invention also relates to the preparation of dye mixtures according to the present invention. This may be effected in a conventional manner, by mechanically mixing the solid or liquid individual dyestuffs of the general formulae 1 and 2 and optionally of the general formulae (3a), (3b) and/or (4) to (10) in the desired blend ratio. The requisite individual dyes of the general formulae (1) to (10) are known and can be prepared according to processes known per se, or else acquired commercially.

[0019] A dyestuff of the general formula (1) may for example be prepared by

a) preparing an aqueous solution of a mixture of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid and a diazo compound prepared by diazotization of a compound of the general formula (11)

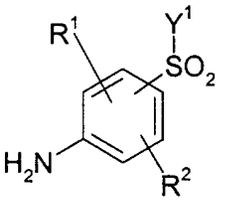


(11)

where R^3, R^4 and Y^2 are each as defined above, and carrying out a coupling reaction, preferably at a pH below 1.5, to form a compound of the formula (3b), and

b) reacting the compound of the formula (3b) obtained in a second coupling reaction, preferably at a pH between

3 and 6.5, with a diazo compound prepared by diazotization of a compound of the general formula (12)

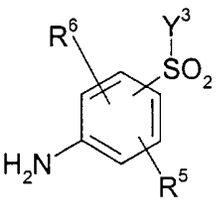


(12)

where R^1, R^2 and Y^1 are each as defined above

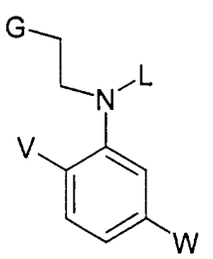
[0020] A dyestuff of the general formula (2) may be prepared likewise by

a) diazotation of a compound of the general formula (13)



(13)

where R^5, R^6 and Y^3 are each as defined above, and
b) coupling the diazo compound obtained from the compound of the general formula (13) with a solution or a suspension of a compound of the general formula (14)



(14)

where G, L, V and W are each as defined above.
The coupling reaction to form a dyestuff of the general formula (2) is preferably carried out at a pH between 3 and 7. The dye mixtures of the present invention may then be produced by mixing the solutions of the dyestuffs of the formulae (1) and (2) obtained, optionally together with the dyestuffs of the general formulae (3a), (3b) and (4) to (10) in the appropriate proportions and isolation by the addition of salt or evaporation of water in, for example, a spray dryer. Alternatively, the individual dyes of the general formulae (1) and (2) can be isolated as powders or press cakes and then mixed, optionally together with the dyestuffs of the general formulae (3a), (3b) and (4) to (10). As mentioned above, the dyestuffs of the general formulae (3a) and (3b) may already be formed during synthesis of the dyestuff of the general forrmula (1).

[0021] Preferred compounds of the general formulae (11), (12) and (13) are 1-sulfo-4-(2-sulfatoethylsulfonyl)-aniline, 1-sulfo-5-(2-sulfatoethylsulfonyl)-aniline, 3-(2-sulfatoethylsulfonyl)-aniline, 2-methoxy-5-(2-sulfatoethylsulfonyl)-aniline, 2,5-dimethoxy-4-(2-sulfatoethylsulfonyl)-aniline, 2-methoxy-5-methyl-4-(2-sulfatoethylsulfonyl)-aniline, 4-(ethenosulfonyl)-aniline and 4-(2-sulfatoethylsulfonyl)-aniline.
[0022] Preferred compounds of the general formula (14) are N,N-bis-(2-hydroxyethyl)-aniline, N,N-bis-(2-hydroxyethyl)-3-toluidine, N,N-bis-(2-hydroxyethyl)-3-N-acetaniline, N,N-bis-(2-hydroxyethyl)-3-aminoaniline, N,N-bis-(2-sulfatoethyl)-aniline, N,N-bis-(2-sulfatoethyl)-toluidine, N,N-bis-(2-sulfatoethyl)-3-chloroaniline, N,N-bis-(2-sulfatoethyl)-

acetaniline, N,N-bis-(2-sulfatoethyl)-3-aminoaniline, N-(2-hydroxyethyl)-N-ethyl-aniline, N-(2-hydroxyethyl)-N-ethyl-3-toluidine, N-hydroxyethyl-N-ethyl-3-acetaniline, N-hydroxyethyl-N-ethyl-3-aminoaniline, N-(2-sulfatoethyl)-N-ethyl-aniline, N-(2-sulfatoethyl)-N-ethyl-toluidine, N-(2-sulfatoethyl)-N-ethyl—3-chloroaniline, N-(2-sulfatoethyl)-N-ethyl-aniline, N-(2-sulfatoethyl)-N-ethyl-3-acetamidoaniline, N-(2-sulfatoethyl)-N-ethyl-3-methoxyaniline, N-(2-sulfatoethyl)-N-ethyl-3,5-dimethoxyaniline, N-(2-sulfatoethyl)-N-(2-cyanoethyl)-aniline, N-(2-sulfatoethyl)-N-(2-cyanoethyl)-toluidine, N-(2-sulfatoethyl)-N-(2-cyanoethyl)—3-acetamidoaniline, N-(2-sulfatoethyl)-N-(2-cyanoethyl)-3-chloroaniline, N-(2-sulfatoethyl)-N-(2-cyanoethyl)-5-methoxy-3-acetamidoaniline, N,N-bis-(2-sulfoethyl)-aniline, N,N-bis-(2-sulfoethyl)-3-toluidine, N,N-bis-(2-sulfoethyl)-3-acetaniline, N,N-bis-(2-hydroxyethyl)-5-methoxy-3-toluidine, N,N-bis-(2-hydroxyethyl)-5-methoxy-3-acetaniline, N,N-bis-(2-hydroxyethyl)-5-methoxy-3-aminoaniline, N,N-bis-(2-sulfatoethyl)-toluidine, N,N-bis-(2-sulfatoethyl)-5-methoxy—3-chloroaniline, N,N-bis-(2-sulfatoethyl)-5-methoxy-3-acetaniline and N,N-bis-(2-sulfatoethyl)-3-aminoaniline.

[0023] Dye mixtures according to the present invention, containing only dyestuffs of the general formulae (1) and (2), whose precursors of the general formulae (11), (12) and (13) are identical ((11) = (12) = (13)) may also be obtained by direct synthesis. This may be effected in a conventional manner by reacting the diazonium salt of the compound of the general formula (11) with a mixture of 1-amino-8-naphthol-3,6-disulfonic acid and a compound of the general formula (14) in the desired blend ratio.

[0024] Dye mixtures of the present invention containing the dyestuffs of the general formulae (1) and (2) and optionally (3a), (3b) and (4) to (10), partly or completely in form of the vinylsulfonyl dyestuff (i.e. the Y-moiety is ethenyl) cannot only be prepared by the above mentioned methods using appropriate vinylsulfonyl starting compounds, but also by reacting dye mixtures of the present invention containing dyestuffs wherein the Y-moieties are $—CH_2CH_2Z$ with Z being chloro, thiosulfato or sulfato, with alkali in an amount necessary to transfer said Y-moieties into ethenyl-groups to the required extent. Said transfer is carried out by generally known methods of transferring β-substituted ethylsulfonyl groups into the vinylsulfonyl group.

[0025] The dye mixtures of the invention have useful application properties. They are used for dyeing or printing hydroxyl- and/or carboxamido-containing materials, for example in the form of sheetlike structures, such as paper and leather or of films, for example composed of polyamide, or in bulk, as for example of polyamide and polyurethane, but especially for dyeing or printing these materials in fiber form.

The present invention thus also relates to the use of the dye mixtures of the invention for dyeing or printing these materials, or rather to processes for dyeing or printing these materials in a conventional manner, by using a dye mixture of the invention as colorant. The materials are preferably employed in the form of fiber materials, especially in the form of textile fibers, such as woven fabrics or yarns, as in the form of hanks or wound packages.

[0026] Hydroxyl-containing materials are those of natural or synthetic origin, for example cellulose fiber materials or their regenerated products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton, but also other vegetable fibers, such as linen, hemp, jute and ramie fibers; regenerated cellulose fibers are for example staple viscose and filament viscose.

[0027] Carboxamido-containing materials are for example synthetic and natural polyamides and polyurethanes, especially in the form of fibers, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11 and nylon-4.

[0028] The dye mixtures of the invention can be applied to and fixed on the substrates mentioned, especially the fiber materials mentioned, by the application techniques known for water-soluble dyes, especially fiber-reactive dyes. For instance, on cellulose fibers they produce dyeings of deep black shades which are readily dischargeable. They have good color build-up properties and good wash-off properties in respect to unfixed dye portions.

[0029] Application is preferably from an aqueous bath at temperatures between 40 and 105°C, optionally at a temperature of up to 130°C under superatmospheric pressure, and optionally in the presence of customary dyeing auxiliaries. One possible procedure is to introduce the material into the warm bath and to gradually heat the bath to the desired dyeing temperature and to complete the dyeing process at that temperature. The neutral salts which accelerate the exhaustion of the dyes may also, if desired, only be added to the bath after the actual dyeing temperature has been reached.

[0030] Similarly, the customary printing processes for cellulose fibers, which can be carried out either single-phase, for example by printing with a print paste comprising sodium bicarbonate or some other acid-binding agent and by subsequent steaming at 100 to 103°C, or two-phase, for example by printing with a neutral or weakly acidic print colour and subsequent fixation either by passing the printed material through a hot electrolyte-comprising alkaline bath or by overpadding with an alkaline electrolyte-comprising padding liquor with subsequent batching of the alkali-overpadded material or subsequent steaming or subsequent treatment with dry heat, produce strong prints with well-defined contours and a clear white ground. The appearance of the prints is not greatly affected by variations in the fixing conditions.

[0031] When fixing by means of dry heat in accordance with the customary thermofix processes, hot air from 120 to 200°C is used. In addition to the customary steam at 101 to 103°C it is also possible to use superheated steam and highpressure steam at temperatures of up to 160°C.

[0032] The acid-binding agents which effect the fixation of the dyes of the dye mixtures of the invention on the cellulose fibers include for example water-soluble basic salts of the alkali metals and likewise alkaline earth metals of inorganic or organic acids or compounds which liberate alkali in the heat. Especially suitable are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids, the preferred alkali metal compounds being the sodium and potassium compounds. Such acid-binding agents include for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate.

[0033] The dye mixtures of the invention are notable for a high yield of fixation when applied to the cellulose fiber materials by dyeing or printing. The cellulose dyeings obtained following the customary aftertreatment by rinsing to remove unfixed dye portions exhibit excellent wetfastnesses, in particular since such unfixed dye portions are easily washed off on account of their good solubility in cold water.

[0034] Furthermore, the dye mixtures of the invention can also be used for the fiber-reactive dyeing of wool. Moreover, wool which has been given a nonfelting or low-felting finish (cf. for example H. Rath, Lehrbuch der Textilchemie, Springer-Verlag, 3rd Edition (1972), p. 295-299, especially the finish by the Hercosett process (p. 298); J. Soc. Dyers and Colourists 1972, 93-99, and 1975, 33-44) can be dyed with very good fastness properties.

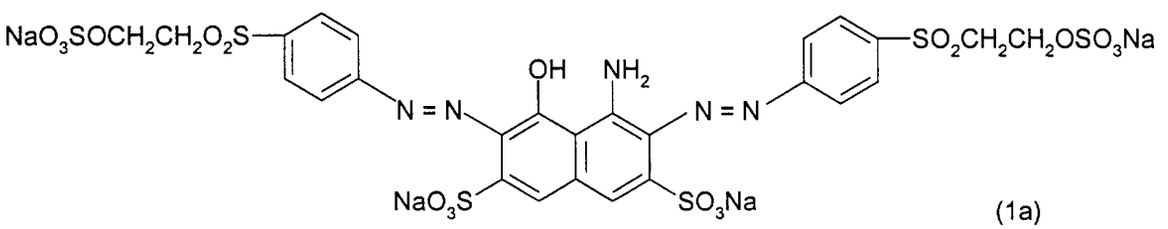
[0035] The process of dyeing on wool is here carried out in a conventional manner from an acidic medium. For instance, acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate may be added to the dyebath to obtain the desired pH. To obtain a dyeing of acceptable levelness, it is advisable to add a customary leveling agent, for example on the basis of a reaction product of cyanuric chloride with 3 times the molar amount of an aminobenzenesulfonic acid and/or of an aminonaphthalenesulfonic acid or on the basis of a reaction product of for example stearylamine with ethylene oxide. For instance, the dye mixture of the invention is preferably subjected to the exhaust process initially from an acidic dyebath having a pH of about 3.5 to 5.5 under pH control and the pH is then, toward the end of the dyeing time, shifted into the neutral and optionally weakly alkaline range up to a pH of 8.5 to bring about, especially for very deep dyeings, the full reactive bond between the dyes of the dye mixtures of the invention and the fiber. At the same time, the dye portion not reactively bound is removed.

[0036] The procedure described herein also applies to the production of dyeings on fiber materials composed of other natural polyamides or of synthetic polyamides and polyurethanes. In general, the material to be dyed is introduced into the bath at a temperature of about 40°C, agitated therein for some time, the dyebath is then adjusted to the desired weakly acidic, preferably weakly acetic acid, pH and the actual dyeing is carried out at a temperature between 60 and 98°C. However, the dyeings can also be carried out at the boil or at temperatures of up to 120°C (under superatmospheric pressure).

[0037] The examples which follow illustrate the invention. Parts and percentages are by weight, unless otherwise stated. The parts by weight bear the same relation to parts by volume as the kilogram to the liter.

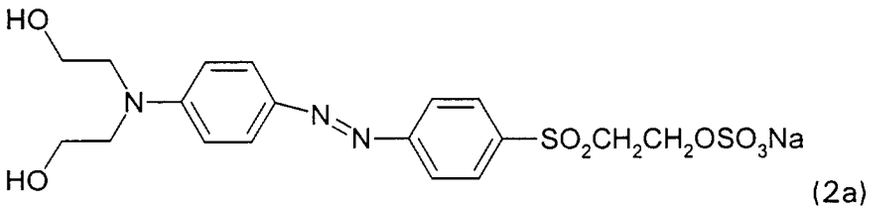
Example 1

[0038] 200 parts of an electrolyte-containing dye powder which contains the navydyeing disazo dyestuff of the formula (1a)



(1a)

in a proportion of 70% are mechanically mixed with 60 parts of an electrolyte-containing dye powder which contains the orange-dyeing monoazo dyestuff of the formula (2a)



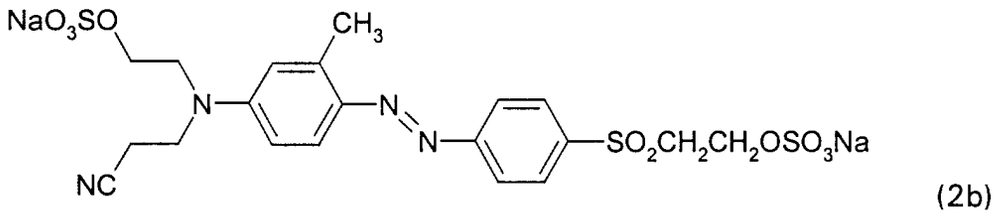
(2a)

in a proportion of 70%.

[0039] The resulting dye mixture according to the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces for example on cellulose fiber materials dyeings and prints in deep black shades.

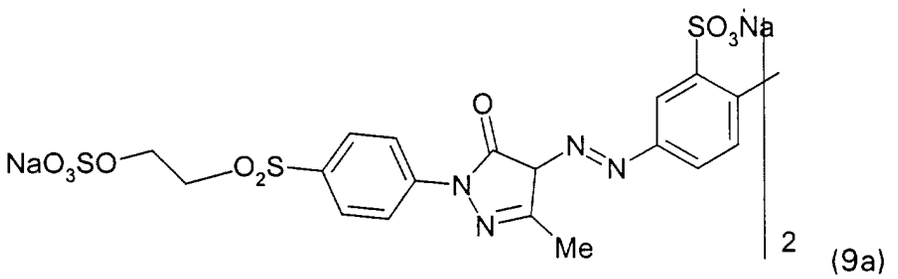
Example 2

[0040] A dye mixture according to the invention is prepared by diazotizing 281 parts of 4-(β-sulfatoethylsulfonyl) aniline in 1500 parts of ice-water and 180 parts of 30 % aqueous hydrochloric acid with 173 parts of 40 % strength aqueous sodium nitrite solution. 120 parts of 1-amino-8-napthol-3,6-disulfonic acid is added and coupling is carried out at a pH between 1 and 1.3 and at a temperature below 20°C (the pH is maintained with about 50 parts of sodium bicarbonate). 88 parts N-(β-cyanoethyl)-N-(2-sulfatoethyl)-3-toluidine is added to the above coupling mixture and the pH is raised to 6 with sodium carbonate at a temperature below 30°C. The resulting solution contains the dyestuffs of the formulae (1a) and (2b)



(2b)

[0041] To this solution containing the dyestuffs of the formulae (1a) and (2b) 50 parts of a yellow dye of the formula (9a)



(9a)

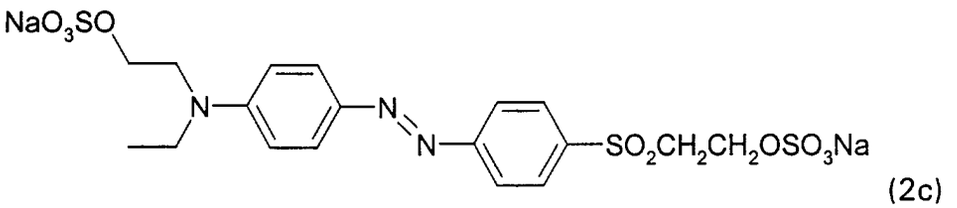
are added, which was prepared according to DE-C 1215282. The result obtained is dye mixture in which the dyestuffs of the formulae (1a), (2b) and (9a) are present in the ratio of about 70 % : 24 % : 7 %.

[0042] This dye solution is adjusted to pH 4.5 by adding 5 parts of a sodium phosphate buffer. By further diluting with water or by evaporating the solution, this liquid dye mixture can then be standardized to the desired strength for a liquid preparation. The dye mixture affords deep black shades on cellulosic materials.

Examples 3

[0043] 281 parts of 4-(β-sulfatoethylsulfonyl)aniline in 1500 parts of ice-water and 180 parts of 30 % aqueous hydrochloric acid was diazotized by dropwise addition of 173 parts of 40% aqueous sodium nitrite solution. After stirring for 4 hours at 0-5°C excess nitrite was removed by addition of sulfamic acid. The resulting solution was pumped to a

neutral solution of 245 parts N-ethyl-N-(2-sulfatoethyl)-aniline in 1500 parts water and the pH was maintained at 4 to 6 with sodium carbonate at a temperature below 30°C. The resulting solution was spray dried yielding approx. 700 parts of the dyestuff (2c):

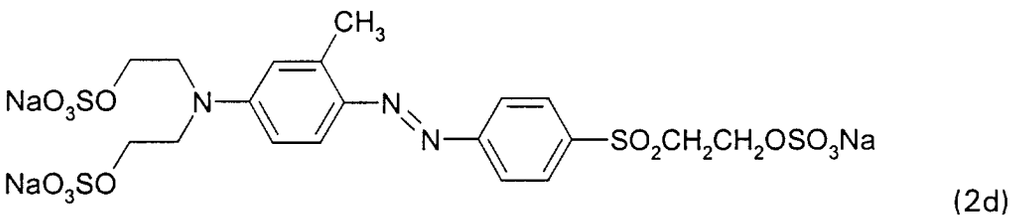


(2c)

22,5 parts of the dyestuff thus obtained where mixed with 77.5 parts of dyestuff (1a), which was prepared according to the literature, in a mechanical blender. The resulting mixture dyes cotton in deep black shades.

Examples 4 to 177

[0044] The following orange components where prepared as described in Example 3:



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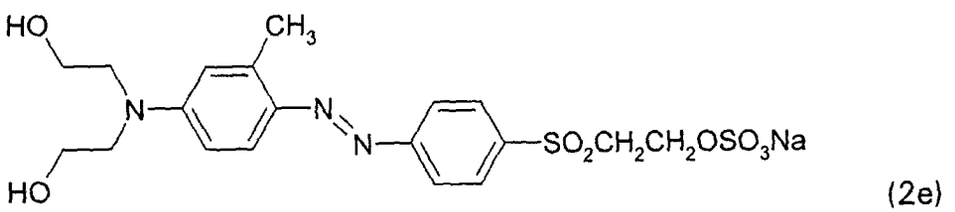

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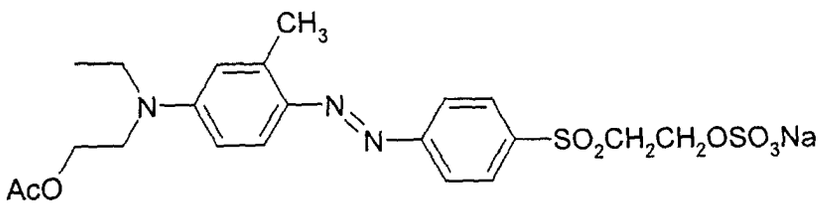

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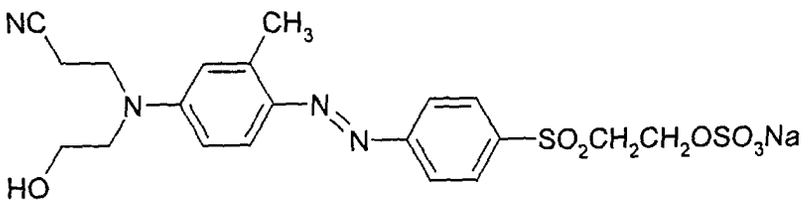

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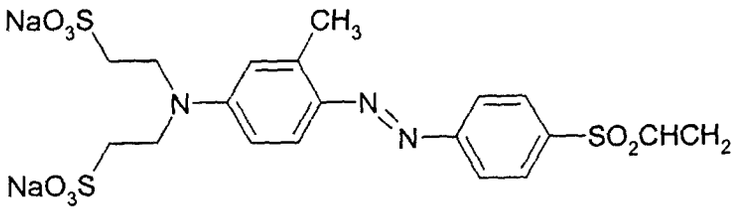

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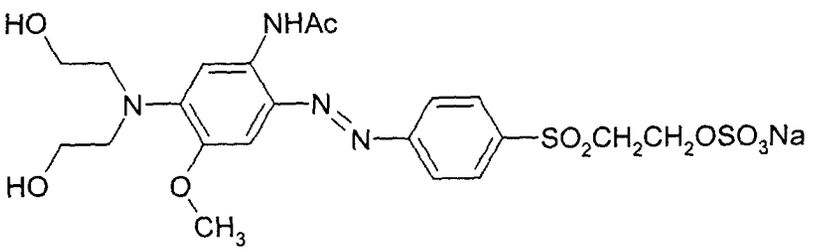

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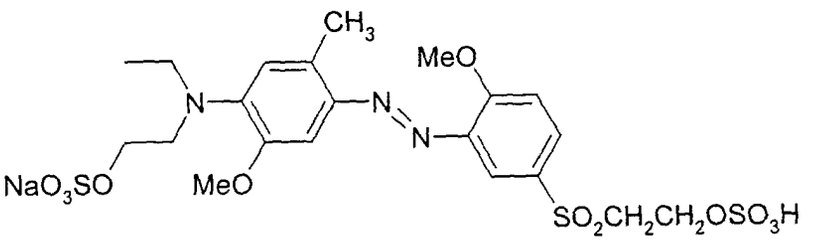

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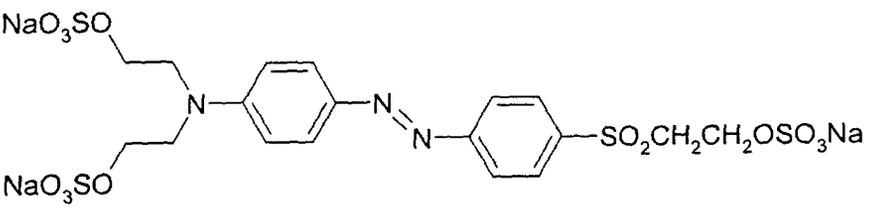

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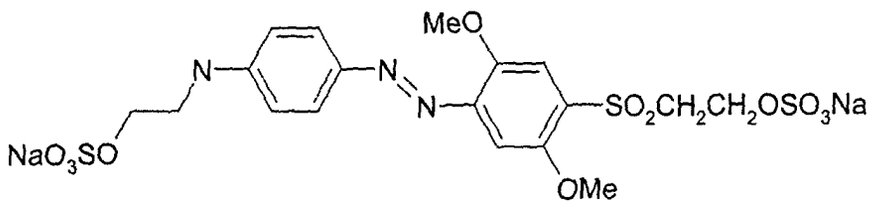

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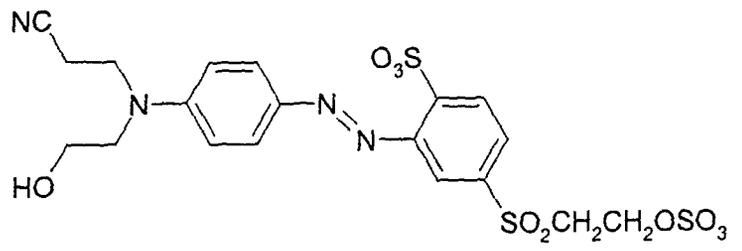

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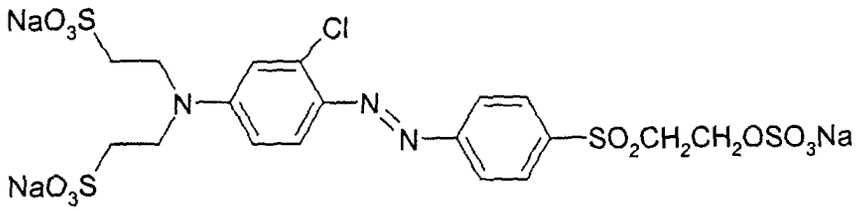

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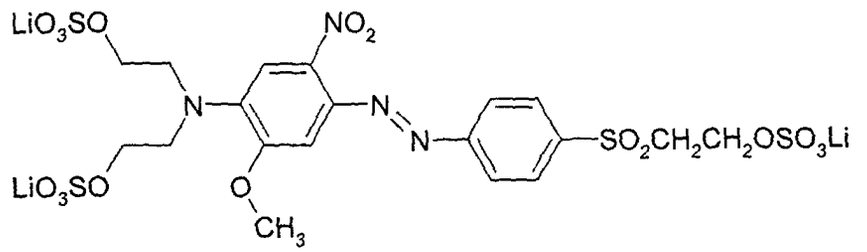

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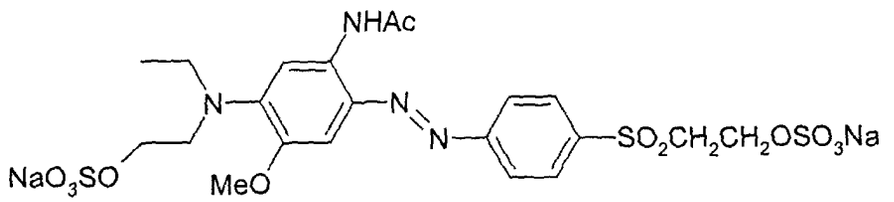

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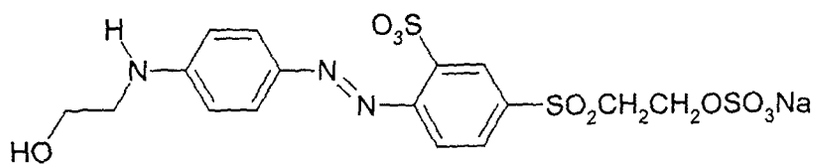

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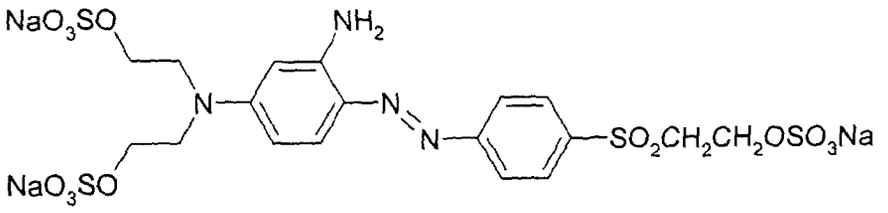

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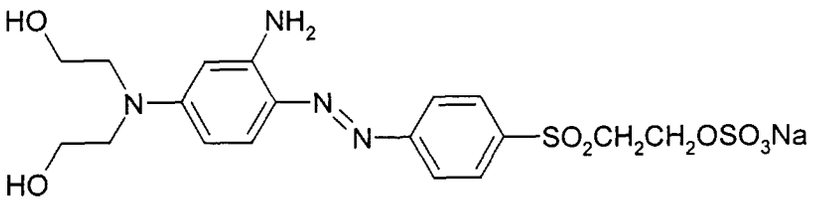

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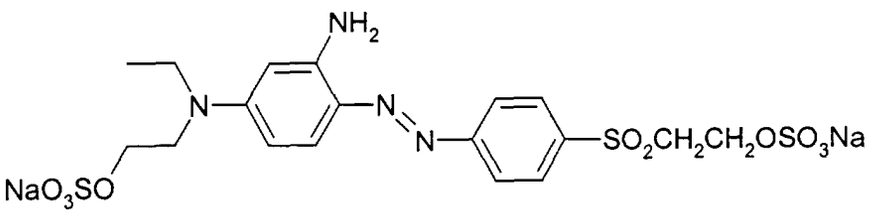

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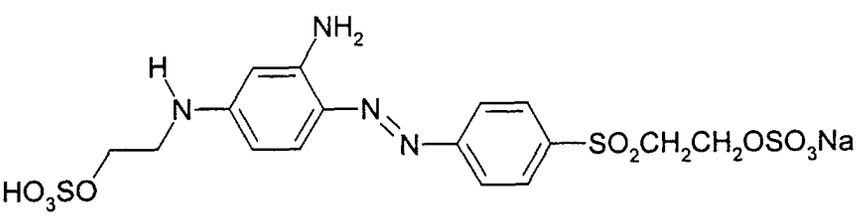

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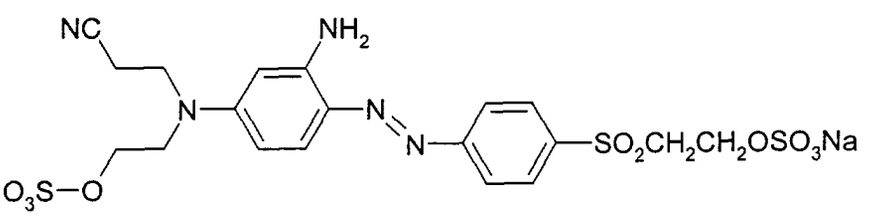

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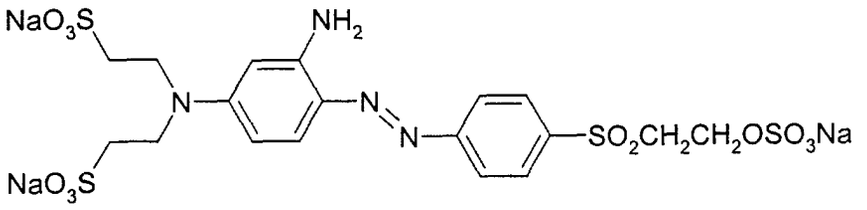

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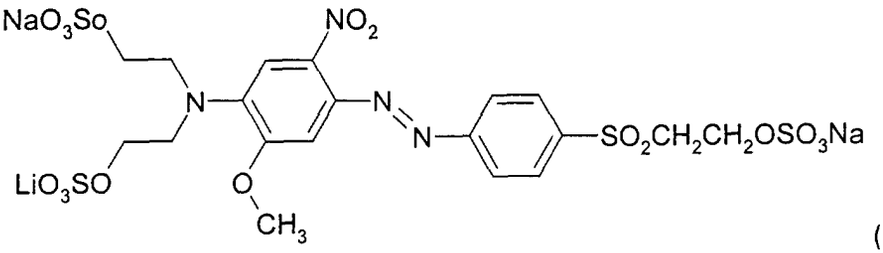

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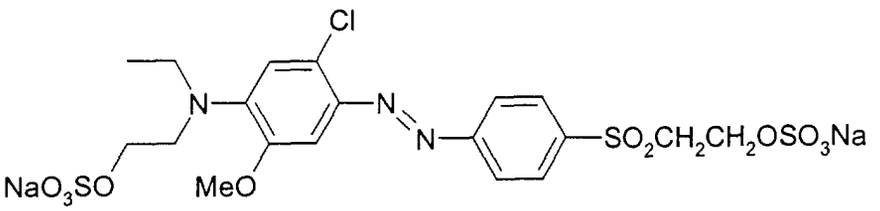

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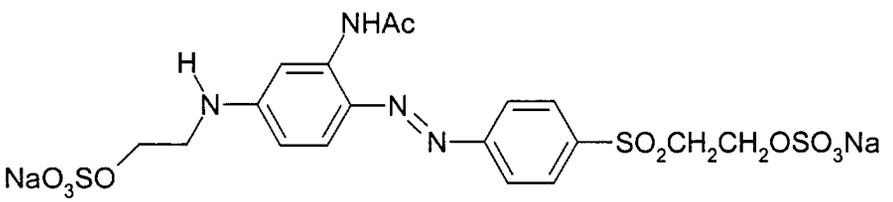

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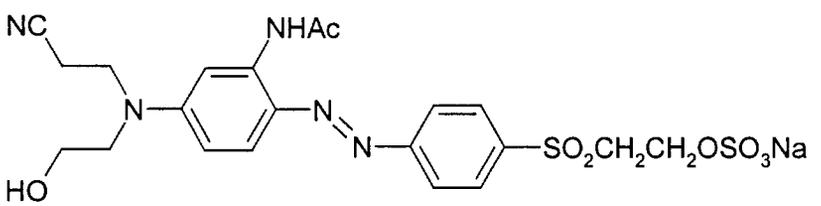

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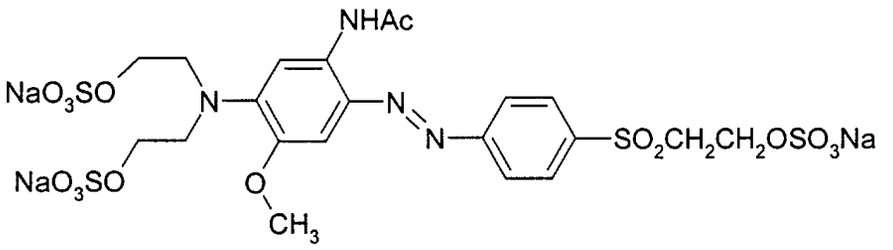

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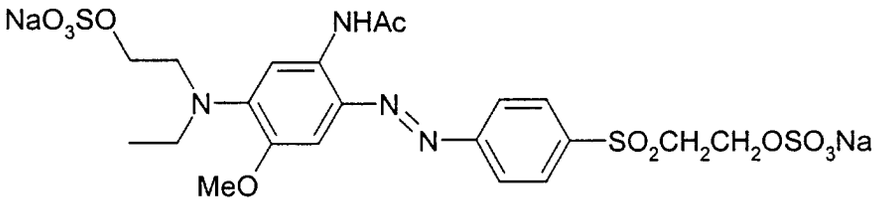

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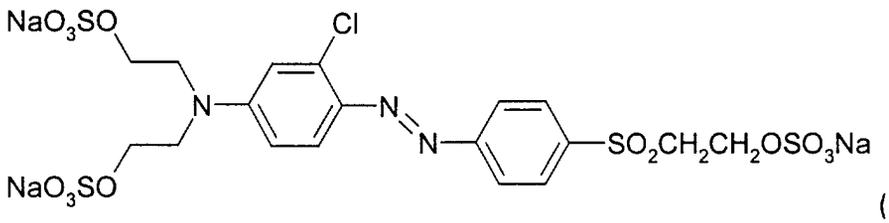

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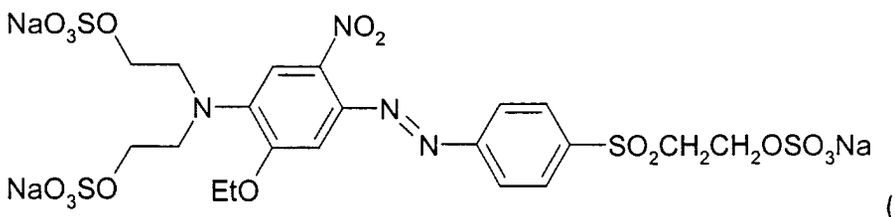

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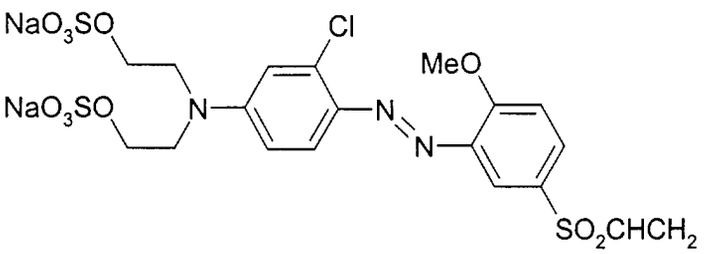

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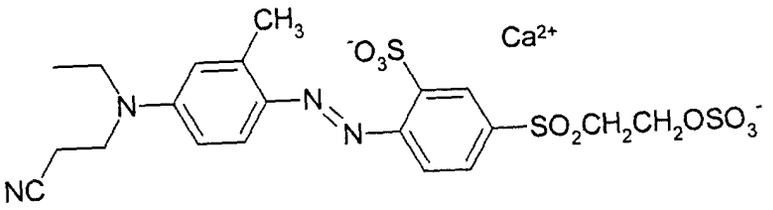
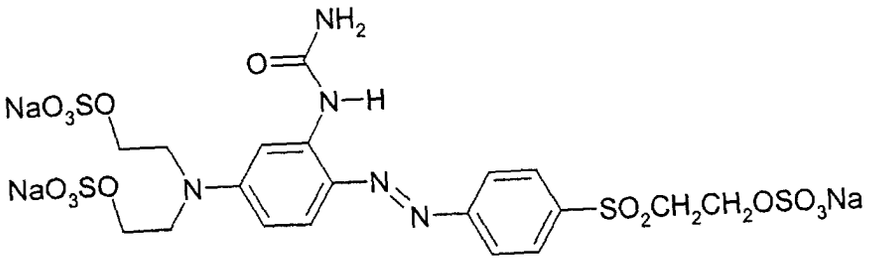
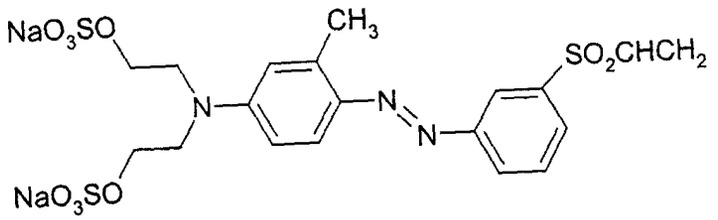


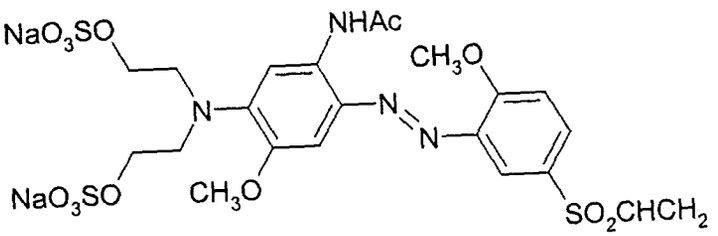
(2ag)



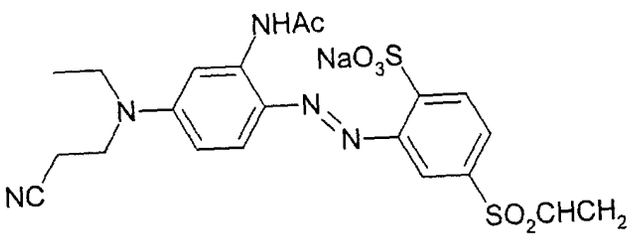
(2ah)



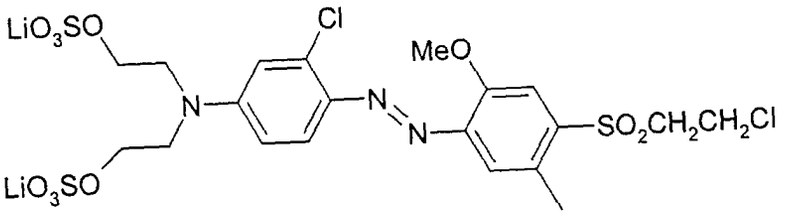
(2ai)



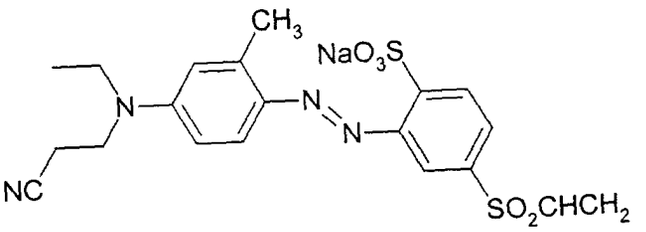
(2aj)



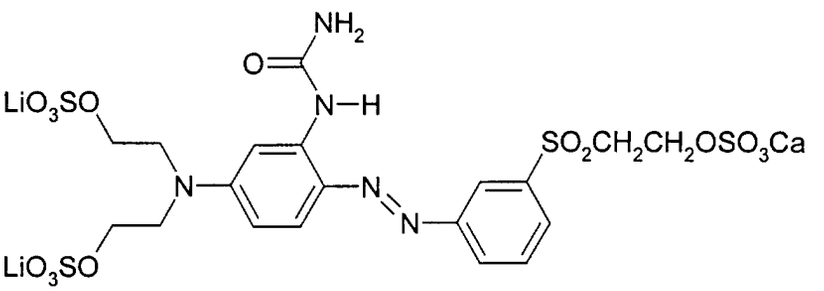
(2ak)



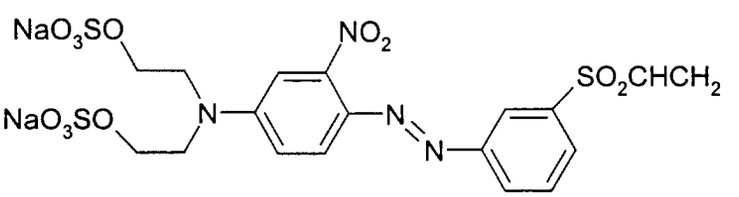
(2al)



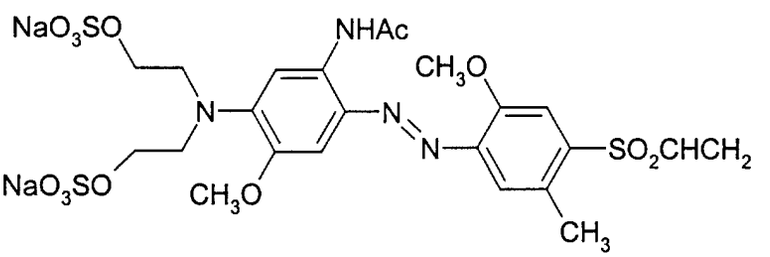
(2am)



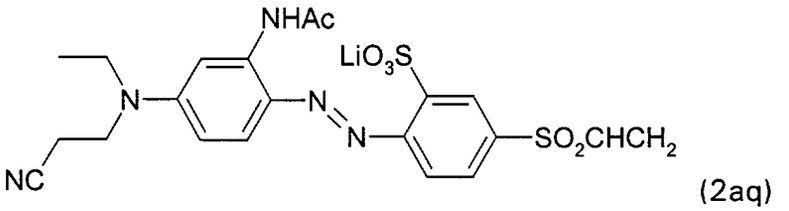
(2an)



(2ao)

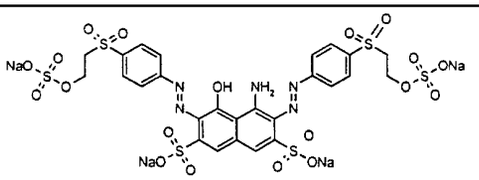


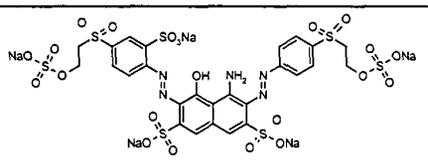
(2ap)

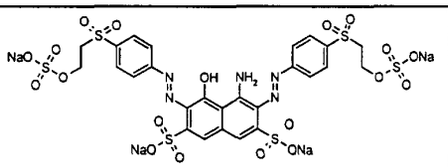


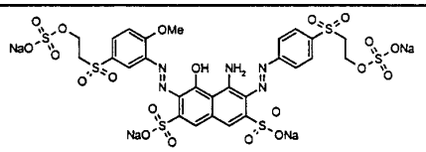
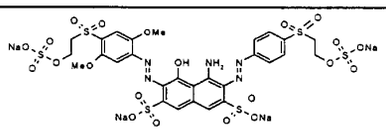
(2aq)

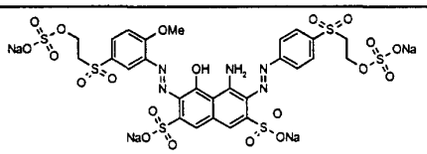
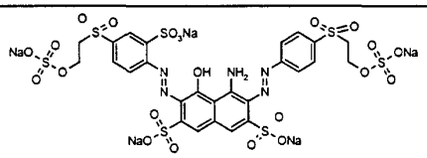
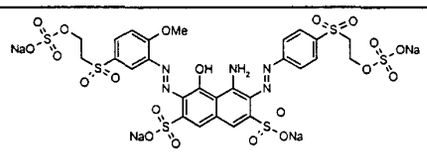
[0045] The dyestuffs (2d) to (2aq) were mixed with dyestuffs of the general formula (1) and optionally with an additional dyestuff of the formulae (3a), (3b) and (4) to (10) as specified in the following table. When employed according to the application and fixing methods customary in the art for fiber-reactive dyes, these dye mixtures produce, for example, on cellulose fiber materials, deep black dyeings.

Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
4		2a	75 : 25

Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
5	Ditto	2d	70 : 30
6	Ditto	Ditto	80 : 20
7	Ditto	2e	75 : 25
8	Ditto	Ditto	70 : 30
9	Ditto	Ditto	80 : 20
10	Ditto	2j	75 : 25
11	Ditto	Ditto	70 : 30
12	Ditto	Ditto	80 : 20
13	Ditto	2i	75 : 25
14	Ditto	Ditto	70 : 30
15	Ditto	Ditto	80 : 20
16	Ditto	2h	75 : 25
17	Ditto	Ditto	70 : 30
18	Ditto	Ditto	80 : 20
19	Ditto	2f	77.5 : 22.5
20	Ditto	2g	77.5 : 22.5
21		2a	75 : 25
22	Ditto	Ditto	70 : 30
23	Ditto	Ditto	80 : 20
24	Ditto	2d	75 : 25
25	Ditto	Ditto	70 : 30
26	Ditto	Ditto	80 : 20
27	Ditto	2e	75 : 25
28	Ditto	Ditto	70 : 30
29	Ditto	Ditto	80 : 20
30	Ditto	2j	75 : 25
31	Ditto	Ditto	70 : 30

Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
32	Ditto	Ditto	80 : 20
33	Ditto	2i	75 : 25
34	Ditto	Ditto	70 : 30
35	Ditto	Ditto	80 : 20
36	Ditto	2h	75 : 25
37	Ditto	Ditto	70 : 30
38	Ditto	Ditto	80 : 20
39	Ditto	2f	77.5 : 22.5
40	Ditto	2g	77.5 : 22.5
41		2k	75 : 25
42	Ditto	2l	70 : 30
43	Ditto	2m	ditto
44	Ditto	2n	Ditto
45	Ditto	2o	Ditto
46	Ditto	2p	Ditto
47	Ditto	2q	Ditto
48	Ditto	2r	Ditto
49	Ditto	2s	Ditto
50	Ditto	2t	Ditto
51	Ditto	2u	Ditto
52	Ditto	2v	Ditto
53	Ditto	2w	Ditto
54	Ditto	2x	Ditto
55	Ditto	2y	Ditto
56	Ditto	2z	Ditto
57	Ditto	2aa	Ditto
58	Ditto	2ab	Ditto

Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
59	Ditto	2ac	Ditto
60	Ditto	2ad	Ditto
61		2k	75 : 25
62	Ditto	2l	70 : 30
63	Ditto	2m	Ditto
64	Ditto	2n	Ditto
65	Ditto	2o	Ditto
66	Ditto	2p	Ditto
67	Ditto	2q	Ditto
68	Ditto	2r	Ditto
69	Ditto	2s	Ditto
70	Ditto	2t	Ditto
71	Ditto	2u	Ditto
72	Ditto	2v	Ditto
73	Ditto	2w	Ditto
74	Ditto	2x	Ditto
75	Ditto	2y	Ditto
76	Ditto	2z	Ditto
77	Ditto	2aa	Ditto
78	Ditto	2ab	Ditto
79	Ditto	2ac	Ditto
80	Ditto	2ad	Ditto
81		2ae	75 : 25
82	Ditto	2af	70 : 30
83	Ditto	2ag	ditto
84	Ditto	2ah	Ditto

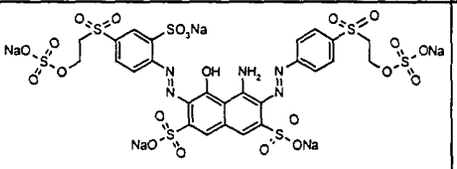
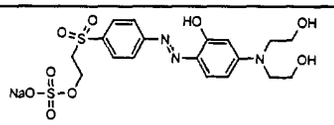
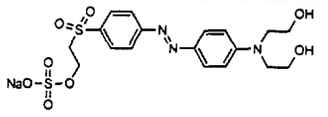
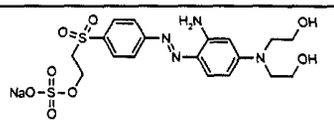
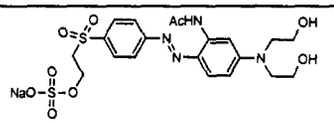
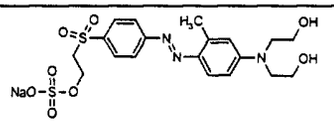
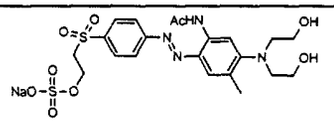
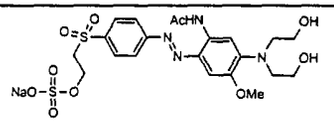
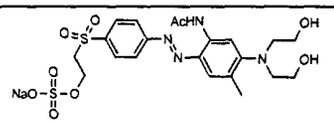
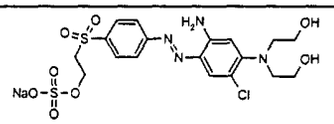
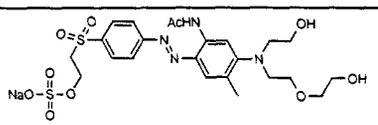
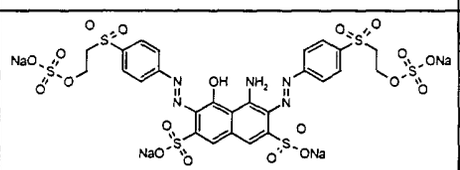
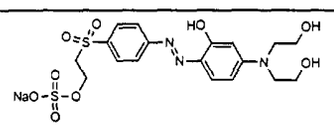
Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
85	Ditto	2ai	Ditto
86	Ditto	2aj	Ditto
87	Ditto	2ak	Ditto
88	Ditto	2al	Ditto
89	Ditto	2am	Ditto
90	Ditto	2an	Ditto
91	Ditto	2ao	Ditto
92	Ditto	2ap	Ditto
93	Ditto	2aq	Ditto
94		2ae	Ditto
95	Ditto	2af	Ditto
96	Ditto	2ag	Ditto
97	Ditto	2ah	Ditto
98	Ditto	2ai	Ditto
99	Ditto	2aj	Ditto
100		2ak	ditto
101	Ditto	2al	70 : 30
102	Ditto	2am	ditto
103	Ditto	2an	Ditto
104	Ditto	2ao	Ditto
105	Ditto	2ap	Ditto
106	Ditto	2aq	Ditto
107		2aj	80 :20

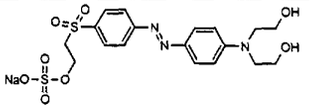
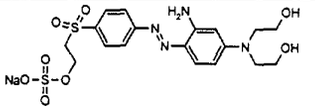
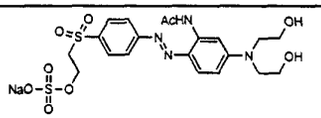
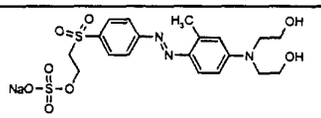
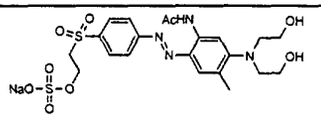
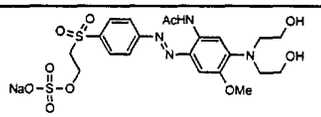
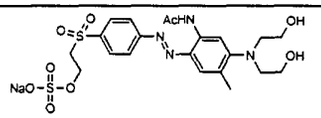
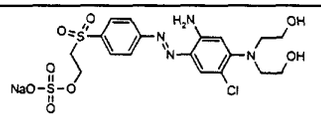
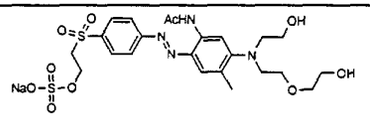
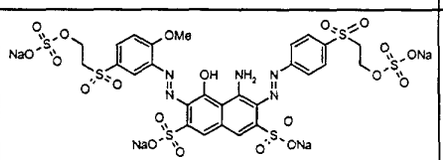
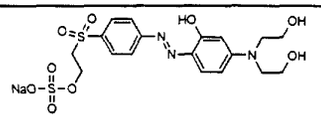
Example	Dyestuff of the formula (1)	Dyestuff of the formula (2)	Ratio
108	Ditto	2af	70 :30
109	Ditto	2i	75 :25

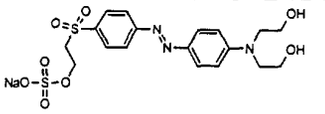
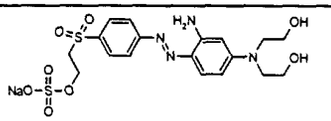
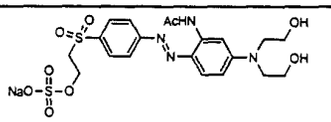
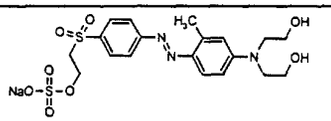
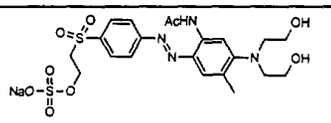
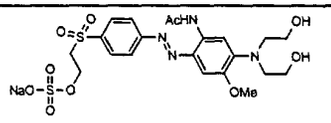
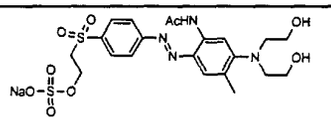
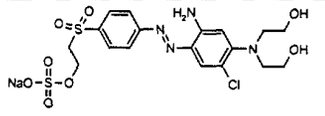
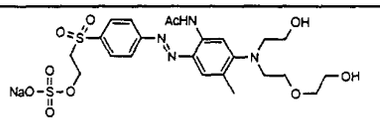
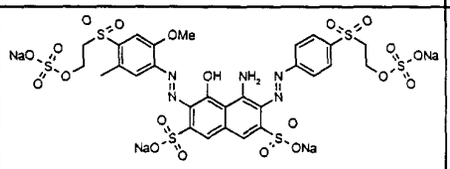
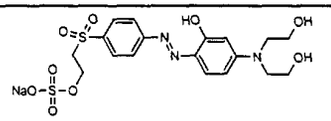
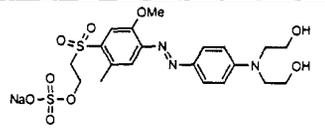
Example	Dye of the formula (1)	Dye of the formula (2)	shading dye	Ratio
110		2d		65 : 20 :15
111	Ditto	2i	ditto	75 : 15 :10
112	Ditto	2k	Ditto	85 : 10 : 15
113	Ditto	2ad	Ditto	70 : 20 : 10
114	Ditto	Ditto		75 : 15 :10
115	Ditto	2t	ditto	ditto
116	Ditto	2r	Ditto	Ditto
117	Ditto	2d	Ditto	Ditto
118	Ditto	Ditto		Ditto
119	Ditto	2p	Ditto	75:20 :5
120	ditto	2ab	Ditto	73 :12 : 10

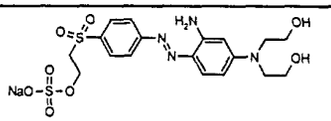
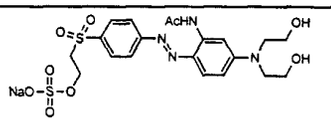
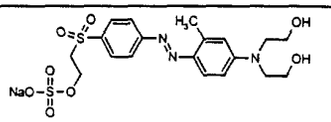
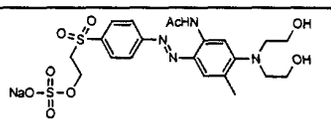
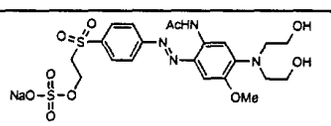
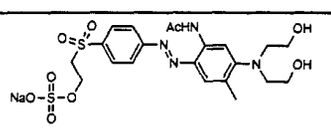
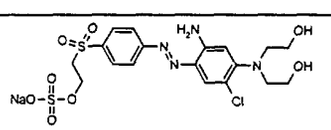
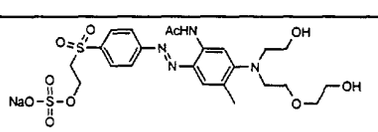
Example	Dye of the formula (1)	Dye of the formula (2)	Shading dye	Ratio
121		2i		65 : 20 :15
122	Ditto	2t	ditto	75 : 15 :10
123	Ditto	2y	Ditto	85 : 10 : 15
124	Ditto	2ac	Ditto	70 : 20 : 10
125		2af		70 : 15 :15
129	Ditto	2ap		Ditto
130	Ditto	2ao	Ditto	75:20 :5

Example	Dye of the formula (1)	Dye of the formula (2)	Shading dye	Ratio
131		2al		65 : 20 :15
132	Ditto	2an	ditto	75 : 15 :10
133	Ditto	2aj	Ditto	85 : 10 : 15
134	Ditto	2ac	Ditto	70 : 20 : 10
135	Ditto	2af		70 : 15 :15
136	Ditto	2ak		Ditto
137	Ditto	2e	Ditto	75:20 :5

Example	Dye of the formula (1)	Dye of the formula (2)	Ratio
138			75 : 25
139	Ditto		Ditto
140	Ditto		Ditto
141	Ditto		Ditto
142	Ditto		Ditto
143	Ditto		Ditto
144	Ditto		Ditto
145	Ditto		80 :20
146	Ditto		70 :30
147	Ditto		75 :25
148			77 : 23

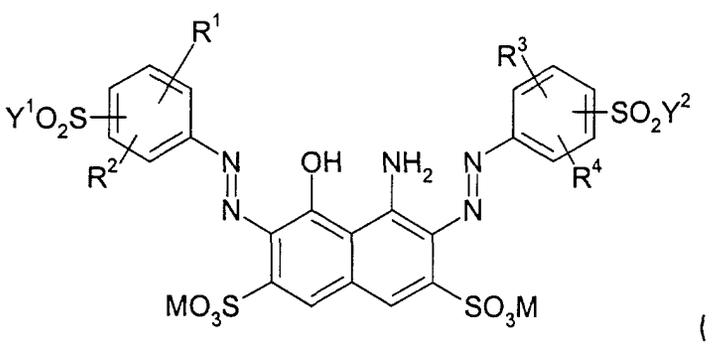
Example	Dye of the formula (1)	Dye of the formula (2)	Ratio
149	Ditto		Ditto
150	Ditto		Ditto
151	Ditto		Ditto
152	Ditto		Ditto
153	Ditto		Ditto
154	Ditto		Ditto
155	Ditto		80 :20
156	Ditto		70 :30
157	Ditto		75 :25
158			77,5 : 22,5

Example	Dye of the formula (1)	Dye of the formula (2)	Ratio
159	Ditto		Ditto
160	Ditto		Ditto
161	Ditto		Ditto
162	Ditto		Ditto
163	Ditto		Ditto
164	Ditto		Ditto
165	Ditto		80 :20
166	Ditto		70 :30
167	Ditto		75 :25
168			75 : 25
169	Ditto		Ditto

Example	Dye of the formula (1)	Dye of the formula (2)	Ratio
170	Ditto		Ditto
171	Ditto		Ditto
172	Ditto		Ditto
173	Ditto		Ditto
174	Ditto		Ditto
175	Ditto		80 :20
176	Ditto		70 :30
177	Ditto		75 :25

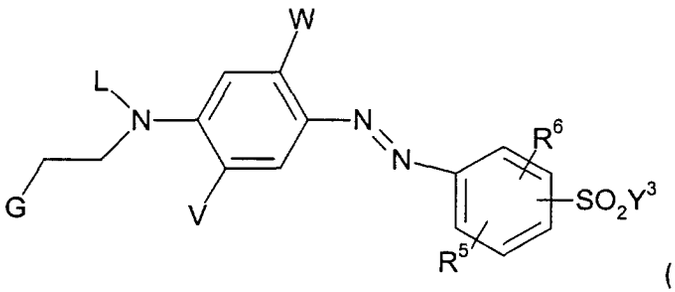
Claims

1. A dye mixture comprising at least one dyestuff of the general formula (1)



(1)

and at least one dyestuff of the general formula (2)



(2)

where

M	is an alkali metal, an ammonium or the equivalent of an alkaline earth metal;
Y^1, Y^2 and Y^3	are independently ethenyl or a grouping of the formula $-CH_2CH_2Z$,

where

Z	is an alkali-eliminable grouping;
R^1, R^2, R^3, R^4, R^5 and R^6	are independently hydrogen, $(C_1$-$C_4)$-alkyl, $(C_1$-$C_4)$-alkoxy, sulfo or chloro;
W	is hydrogen, chloro, bromo, nitro, amino, acetamido, benzamido, $(C_1$-$C_4)$-alkyl, $(C_1$-$C_4)$-alkoxy, hydroxy, ureido or $(C_2$-$C_4)$-alkanoyl;
V	is hydrogen, chloro, bromo, nitro, amino, acetamido, benzamido, $(C_1$-$C_4)$-alkyl, $(C_1$-$C_4)$-alkoxy, hydroxy, ureido or $(C_2$-$C_4)$-alkanoyl;
L	is hydrogen, methyl, ethyl or is ethyl which is substituted in the β-position by G;
G	is cyano, hydroxy, sulfo, sulfato, phosphato, acetyloxy or a residue of a lower polyethylenepolyether.

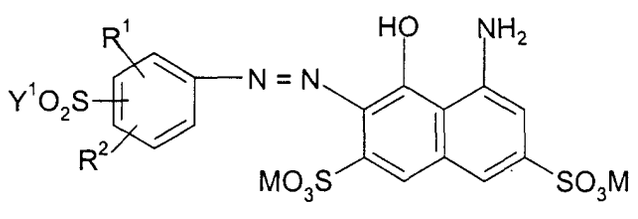
2. A dye mixture as claimed in claim 1 including from 60 to 99%by weight of one or more dyestuffs of the general formula (1) and from 1 to 40%by weight of one or more dyestuffs of the general formula (2), based on the weight of the dye mixture.

3. A dye mixture as claimed in claim 1 and/or 2, including from 65 to 90%by weight of one or more dyestuffs of the general formula (1) and from 10 to 35%by weight of one or more dyestuffs of the general formula (2), based on the weight of the dye mixture.

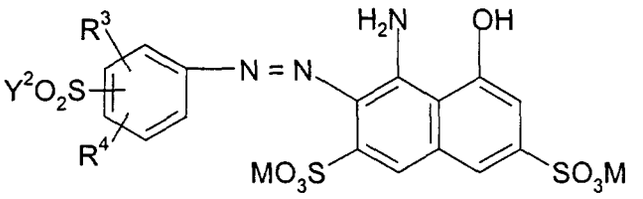
4. A dye mixture as claimed in claim 1 and/or 2, wherein R^1 is hydrogen, methoxy or sulfo, R^2 is hydrogen or methoxy, R^3 and R^4 are hydrogen and R^5 and R^6 are hydrogen, methoxy or sulfo.

5. A dye mixture as claimed in claim 1 and/or 2, wherein W is hydrogen, chloro, nitro, amino, acetamido, methyl or ureido, V is hydrogen or methoxy, L is hydrogen, ethyl, β-sulfatoethyl, β-hydroxyethyl or β-cyanoethyl and G is sulfato, hydroxy or cyano.

6. A dye mixture as claimed in claim 1 and/or 2, additionally containing one or more dyestuffs of the general formulae (3a) or (3b) or both



(3a)

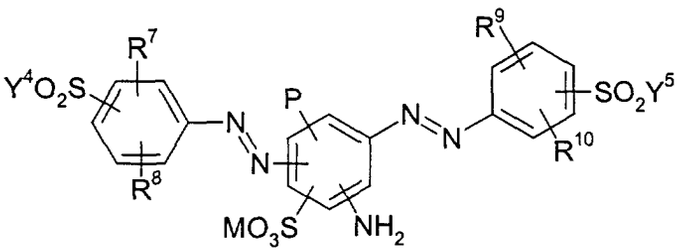


(3b)

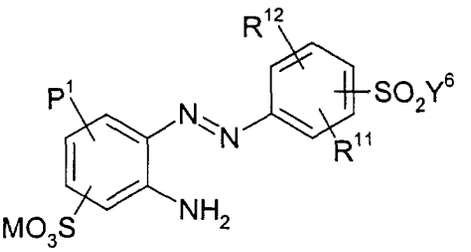
in which R^1, R^2, R^3, R^4, M, Y^1 and Y^2 are defined as given in claim 1.

7. A dye mixture as claimed in claim 1 and/or 2, additionally containing dyestuffs acting as shading components.

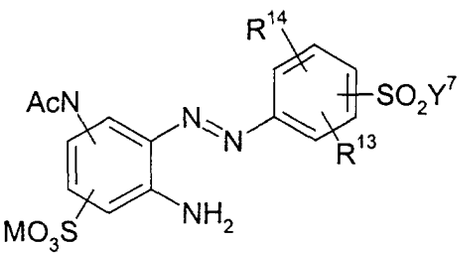
8. A dye mixture as claimed in claim 7, wherein the shading components are dyestuffs of the general formulae (4) to (10)



(4)



(5)



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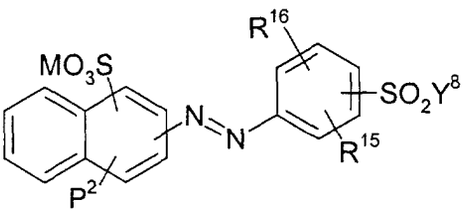

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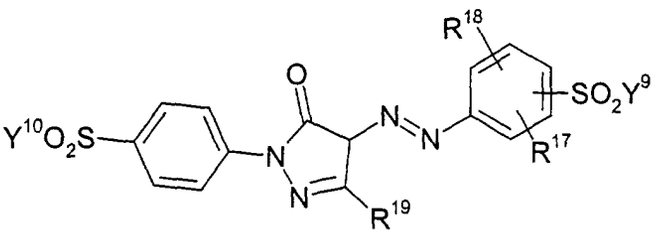

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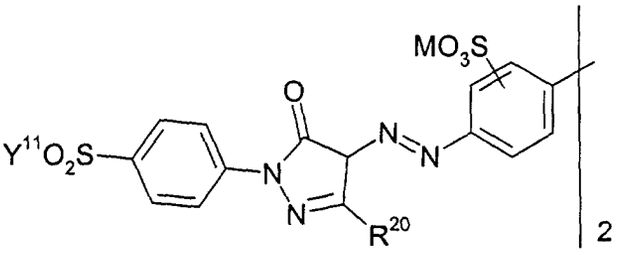
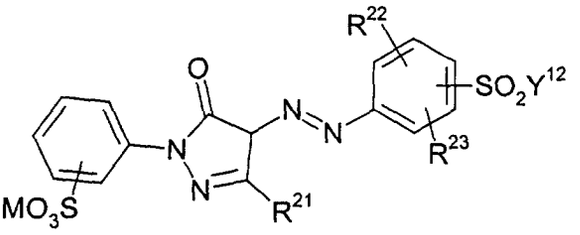


(9)



(10)

where

M	is defined as given in claim 1;
Y^4 to Y^{12}	independently have one of the meanings of Y^1;
R^7 to R^{18} and R^{22} and R^{23}	independently have one of the meanings of R^1;
R^{19} to R^{21}	are independently (C_1-C_4)-alkyl, -COOH or -$COOR^{24}$, where
R^{24}	is (C_1-C_4)-alkyl; and

P to P^2 are independently hydroxy, (C_1-C_4)-alkoxy, amino, (C_1-C_4)-alkylamino or di-(C_1-C_4)-alkylamino.

9. A dye mixture as claimed in claim 7 and/or 8, wherein the shading component is contained in amounts of 0,5 to 20%by weight, based on the weight of the dye mixture.

10. A process for preparing a dye mixture as claimed in one or more of claims 1 to 9, which comprises mechanically mixing the dyestuffs of the general formulae (1) an (2) and optionally (3a), (3b) and (4) to (10) in the desired blend ratio.

11. The method of using a dye mixture as claimed in one or more of claims 1 to 9 for dyeing and printing hydroxyl- and/or carboxamido-containing material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 5676

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	WO 01 00736 A (BASF AG ;ZAMPONI ANDREA MARIA (DE)) 4 January 2001 (2001-01-04) * abstract * * page 56; example 73 * * page 41, line 8 - line 12 *	1-10	C09B67/22 C09B62/507
D,A	KR 9 402 560 B (KYUNGIN SYNTHETIC CORP) 25 March 1994 (1994-03-25) * the whole document * & DATABASE WPI 'Online! DERWENT PUBLICATIONS LTD., LONDON, GB; XP002122686 * abstract *	1-10	
A	EP 0 679 697 A (HOECHST AG) 2 November 1995 (1995-11-02) * page 7, last paragraph - page 8, line 25 *	1-10	
A D	FR 2 749 314 A (EVERLIGHT CHEM IND CORP) 5 December 1997 (1997-12-05) * abstract; example 5 * & US 5 611 821 A 18 March 1997 (1997-03-18)	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C09B
A	EP 0 668 328 A (HOECHST AG) 23 August 1995 (1995-08-23) * page 2, last paragraph * * page 23, paragraph 1 * * page 34, paragraph 1 *	1-10	
A D	EP 0 600 322 A (HOECHST AG) 8 June 1994 (1994-06-08) * abstract * & US 5 445 654 A 29 August 1995 (1995-08-29)	1-10	
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 July 2001	Dauksch, H

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EUROPEAN SEARCH REPORT

Application Number
EP 01 10 5676

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 982 374 A (DYSTAR TEXTILFARBEN GMBH & CO) 1 March 2000 (2000-03-01) * page 2, last paragraph * ---	1-10	
A	EP 0 731 145 A (HOECHST AG) 11 September 1996 (1996-09-11) * abstract; examples * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

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L : document cited for other reasons

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25-07-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0100736 A	04-01-2001	AU 5420000 A	31-01-2001
KR 9402560 B	25-03-1994	NONE	
EP 0679697 A	02-11-1995	DE 4414320 A	26-10-1995
		BR 9501767 A	21-11-1995
		CN 1118796 A	20-03-1996
		JP 8048902 A	20-02-1996
		PL 308326 A	30-10-1995
FR 2749314 A	05-12-1997	GB 2313842 A,B	10-12-1997
		US 5611821 A	18-03-1997
		DE 19620415 A	20-03-1997
		CH 691061 A	12-04-2001
EP 0668328 A	23-08-1995	DE 4405358 A	24-08-1995
		BR 9500672 A	24-10-1995
		CA 2142742 A	20-08-1995
		CN 1114664 A	10-01-1996
		CZ 9500440 A	15-11-1995
		DE 59508235 D	08-06-2000
		DE 59509231 D	07-06-2001
		DE 59509249 D	13-06-2001
		DE 59509250 D	13-06-2001
		DE 59509326 D	12-07-2001
		EP 0971002 A	12-01-2000
		EP 0978543 A	09-02-2000
		EP 0978544 A	09-02-2000
		EP 0964034 A	15-12-1999
		EP 0969050 A	05-01-2000
		EP 0976794 A	02-02-2000
		EP 0982375 A	01-03-2000
		JP 7304986 A	21-11-1995
		PL 307324 A	21-08-1995
EP 0600322 A	08-06-1994	BR 9304856 A	31-05-1994
		CN 1099052 A	22-02-1995
		CZ 9302542 A	15-06-1994
		DE 59309975 D	20-04-2000
		JP 6263997 A	20-09-1994
		TR 27428 A	21-04-1995
		US 5445654 A	29-08-1995
EP 0982374 A	01-03-2000	US 6106580 A	22-08-2000
		BR 9904074 A	12-09-2000
		JP 2000072980 A	07-03-2000

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0982374 A		TR 9902059 A	21-03-2000
EP 0731145 A	11-09-1996	DE 19508156 A	12-09-1996
		JP 8253697 A	01-10-1996
		TR 960868 A	21-10-1996
		US 5690698 A	25-11-1997

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